

Correlative Structure-Bonding and Stability Studies of Pt/ γ -Al₂O₃ Catalysts

Henry O. Ayoola¹, Qing Zhu¹, Cecile S. Bonifacio¹, Matthew P. McCann¹, Matthew T. Curnan^{1,4}, Stephen D. House¹, Joshua Kas², John J. Rehr², Eric A. Stach³, Wissam A. Saidi⁴, and Judith C. Yang¹

¹. Dept. of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA (USA)

². Dept. of Physics, University of Washington, Seattle, WA (USA)

³. Center for Functional Materials, Brookhaven National Laboratory, Upton, NY (USA)

⁴. Dept. of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA (USA)

Pt supported on gamma-alumina (γ -Al₂O₃) is one of the most important heterogeneous catalysts, with technologically important applications including oil refining and catalytic converters [1]. An important property of this catalyst is its stability. Understanding the bonding interactions between Pt and γ -Al₂O₃ is key as they will influence the shape, dispersion, and ultimately stability of Pt nanoparticles (NPs) [2]. Probing these atomic-scale interactions requires direct correlation between theoretical simulations and experimental measurements, which in turn necessitates a model catalyst. We have synthesized a model system of Pt NPs dispersed on single-crystal γ -Al₂O₃ which enables us to study properties of the catalyst system with enough simplicity to allow direct correlation between experimental results and simulations. Single-crystal γ -Al₂O₃ was synthesized by oxidation of NiAl (110) [3]. 2-3 nm Pt NPs were deposited on the γ -Al₂O₃ surface using electron beam evaporation. Cross-sectional TEM samples of the Pt/ γ -Al₂O₃ were prepared using the focused ion beam (FIB) lift-out technique on an FEI Helios dual beam FIB-SEM. Using this model system, we are studying Pt/ γ -Al₂O₃ bonding and Pt NP stability, both *ex situ* and *in situ*, using cutting-edge microscopy and spectroscopy techniques in combination with theoretical simulations.

A critical first step in the comparison of theoretical simulations to experimental results for Pt/ γ -Al₂O₃ is the accurate description of γ -Al₂O₃. Many crystal structures for γ -Al₂O₃ can be found in the literature. Two of the most commonly cited are the spinel model and the monoclinic model proposed Digne et al. [4]. We have determined that the monoclinic model [4] can be used to accurately simulate the O-K near-edge EELS spectrum, despite the spinel model being more accurate to the true structure of γ -Al₂O₃ [5].

Once we determined that the monoclinic model can be used for γ -Al₂O₃ EELS simulations with reasonable accuracy, we investigated the bonding at the Pt/ γ -Al₂O₃ interface. Aberration-corrected EELS spectra were collected along the Pt/ γ -Al₂O₃ interface at cryo-temperature using a Hitachi HD2700C STEM operated at 200 kV with a Gatan Enfina spectrometer, which revealed a unique pre-peak in the O-K EELS at the interface (Figure 1a). Cryo-temperature (using a Gatan Ultra Low Temperature Double-Tilt (ULTDT) cryo-holder) was used to minimize the effect of beam damage on the EELS spectra. Multiple structures based on the monoclinic γ -Al₂O model were constructed to simulate the Pt/ γ -Al₂O₃ (111) interface using density functional theory (DFT). O-K near-edge EELS were then simulated using FEFF9 for each of these structures and compared with the experimentally obtained EELS spectra. The simulated EELS from the interface model with Pt bonded to a surface Al atom and an O adatom on a vacancy-free site best agreed with the energy and intensity of the O-K edge pre-peak observed in experiment (Figure 1b).

We are now studying the stability of Pt NPs on γ -Al₂O₃ *in situ* using environmental TEM. Preliminary results suggest support-influenced Pt nanoparticle behavior in H₂ and O₂ environments at room temperature; with 1.5 nm Pt NPs rapidly agglomerating under H₂ exposure (Figure 2) and 1.5 nm Pt NPs

dispersing under O₂ exposure. We will study the size and shape dynamics of Pt NPs on γ -Al₂O₃, as well as the role of the interface, during H₂/O₂ exposure using our model system [6].

References:

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 [6] The authors acknowledge financial support from NSF-CHE (1300544) and DOE-BES (DE-FG02-97ER45623), and instrument time at Brookhaven National Laboratory. WAS acknowledges a start-up fund from the Department of Mechanical Engineering and Materials Science at University of Pittsburgh.

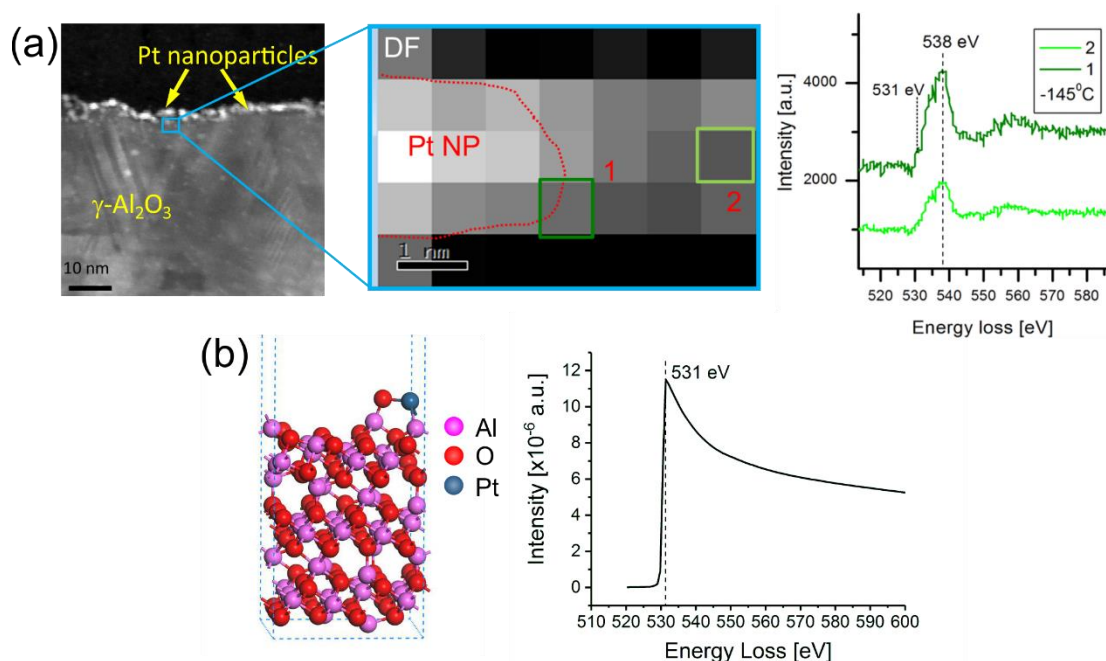


Figure 1. (a) High-angle annular dark-field (HAADF)-STEM image of the Pt/ γ -Al₂O₃ interface. The area of the interface where the spectrum image was acquired is highlighted in blue. Extracted O-K edge EELS spectra from the pixels labeled 1 and 2 are plotted showing the pre-peak in 1 but not in 2. (b) Structural model of the Pt/ γ -Al₂O₃(111) interface developed in DFT and corresponding O-K edge EELS signal from interface O atoms simulated with FEFF9 showing match to pre-peak energy.

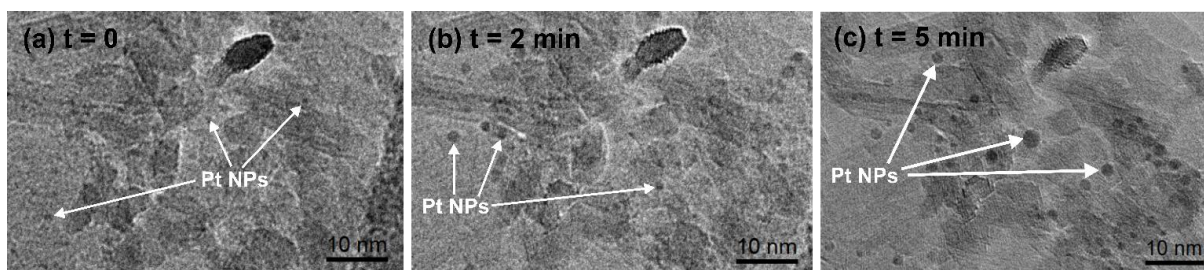


Figure 2. ETEM images of Pt/ γ -Al₂O₃ acquired *in situ* during exposure to 1.2×10^{-2} Pa H₂ at room temperature.